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(54) **Batch process for preparing improved kraft pulp**

Diskontinuierliches Verfahren zur Herstellung von verbesserten Kraft-Zellstoffen

Procédé en discontinu pour préparation des pâtes kraft améliorées

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- **DATABASE WPI Section Ch, Week 8038 Derwent Publications Ltd., London, GB; Class F09, AN 80-66836C XP002042322 & JP 55 103 386 A (SANYO KOKUSAKU PULP CO), 7 August 1980**

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**EP 0 810 321 B1**

## Description

## FIELD OF THE INVENTION

[0001] The present invention relates to a process for preparing kraft pulp in which cellulosic material is treated with recycled pulping process liquids, uncausticized cooking liquor and causticized white liquor for dissolving the lignin therein. More particularly, the present invention relates to the use of green liquor or mother liquor from green liquor carbonate crystallization in early stages of modern displacement kraft batch cooking and the advantage thereof in terms of improved kraft pulp quality.

## BACKGROUND OF THE INVENTION

[0002] In the various kraft pulping processes cellulosic material, wood chips are generally treated at elevated temperatures with alkaline cooking liquor containing sodium hydroxide and sodium hydrogen sulfide, called white liquor. In these processes, cooking liquor that results when the inorganic smelt from the recovery furnace is dissolved in water before causticizing the carbonate to hydroxide is generally referred to as green liquor, causticized green liquor is generally referred to as white liquor and spent cooking liquor is generally referred to as black liquor. Typical compositions of the green and white liquors are given in Table 1.

Table 1.

Typical compositions of the so-called green liquor and white liquor /1/.		
Component	Green Liquor	White Liquor
	Conc. g/l as Na <sub>2</sub> O	Conc. g/l as Na <sub>2</sub> O
NaOH	15	95
Na <sub>2</sub> S	37	38
Na <sub>2</sub> CO <sub>3</sub>	107	26

1. Clayton, D., et al., Chemistry of alkaline pulping, in Pulp and Paper Manufacture, 3rd Edition, Vol. 5, Alkaline Pulping, Grace, T.M., Malcom, E. W., ed., TAPPI, CPPA, 1989. p. 17, 15.

[0003] Noteworthy for the green liquor is the high level of carbonate and the low hydroxide concentration. Particularly important is to note that all reduced sulfur is already in the final and useful form of hydrosulfide, HS<sup>-</sup> ions (Na<sub>2</sub>S dissolved in water). The carbonate/hydroxide combination in green liquor does not provide the high pH necessary for the conventional kraft processes and must be converted to so called "white" liquor by a causticizing process, but it represents an excellent hydrosulfide source rich in alkalinity buffering carbonate.

Previously, cooking with green liquor has only been used for high yield semi-chemical pulping, where the delignification is deliberately poor, pulp still contains most of the lignin and fibers must be liberated by mechanical refining after cooking with green liquor (Vardheim, S., The use of green liquor as cooking liquor in the production of semi-chemical hardwood pulps for fluting, Paperi ja Puu (1967)). These kinds of pulp are not suitable for so-called chemical paper pulps at all, cannot be bleached and find their use in board making.

[0004] From the cooking chemicals point of view, the industrial kraft pulp process has been quite unchanged and undeveloped until recently. While it is true that many different chemicals have been proposed for improving factors such as pulp yield, quality and delignification selectivity, none of these proposals has led to acceptable practical solutions to these objectives because each of them has involved complicated extra equipment, additional process steps, more digester capacity or the use of expensive chemicals external to the pulp mill, that cannot be recovered and regenerated.

Beginning in the 70's, a new trend has appeared to exert increasing environmental pressure on the kraft pulp industry to radically reduce the amounts of environment-polluting effluents. To cut down the organic effluents from pulp bleaching, this requires the kraft cooking to be extended to yield a much lower residual lignin concentration in the pulp than before. Due to the resulting inferior pulp quality when using conventional cooking methods to obtain low residual lignin concentration, modified kraft cooking processes had to be developed. Among other things, this development work uncovered the role of hydrosulfide ions: The concentration of hydrosulfide ion must be high in the early stages of cooking - towards the end of the cooking hydrosulfide is no longer effective. The desired role of the hydroxyl ion was found to be exactly the opposite (Sjöblom, K., et al., "Extended delignification in kraft cooking through improved selectivity", Paperi ja puu 65:4, 227 (1983); Nordén, S. and Teder, A., "Modified kraft processes for softwood bleached-grade pulp", TAPPI Journal 62:7, 49 (1979)). In order to obtain optimal hydrosulfide and hydroxide ion concentration profiles, it has been suggested to prepare white liquors of different sulfidity (Jiang et al., "Improved kraft pulping by controlled

sulfide additions", Proceedings of the 7th International Symposium on Wood and Pulp Chemistry, Beijing, P.R. China, May 25-28, 1993; Teder, A. and Olm, L., "Extended delignification by combination of modified kraft pulping and oxygen bleaching", Paperi ja Puu 63:4a, 315 (1981)). In another study (Andrews, E.K., "Extended delignification of southern pine using novel conceptual approaches within the framework of conventional kraft and oxygen technologies", Ph.D. Thesis, Department of wood and paper science, North Carolina State University, 1982), sulfide-containing liquors have been tried as a pretreatment stage before conventional kraft cooking with white liquor. Better pulp viscosity was found, as theory predicts. Since these kinds of pretreatment require a separate cooking stage at a relatively high temperature (effective alkali charge up to 7% on wood and 135 °C), they will cut away a significant period of production time per digester and require process modifications. The predictable loss of production and the modest advantages have rendered this kind of technology not feasible.

[0005] According to another invention (Tikka, US Pat 5,183,535) the sulfur species found in the spent black liquor can be impregnated into and reacted with the wood chips prior to finalizing the cooking with white liquor.

[0006] Another trend in kraft pulp process development has been the strive for energy efficiency. Therefore, from the early 60's, continuous cooking equipment started to dominate the field. However, from the early 80's, new emerging and rivaling energy efficient kraft batch processes using various kinds of displacement technology started to gain ground again. Characteristic for the displacement kraft batch processes is the recovery of hot black liquor at the end of cooking and reuse of its energy in the subsequent batches. Good examples of this development are processes described in, e.g., Fagerlund, U.S. Pat 4,578,149 and Östman, U.S. Pat. 4,764,251. These inventions do recover the heat of the cooking effectively, but the utilization of the cooking chemicals is far from optimized.

[0007] Further development of the displacement kraft batch cooking involved the combination of energy efficiency and efficient usage of residual and fresh cooking chemicals to achieve facilitated delignification and high pulp strength. This can be accomplished by arranging the displacement at the end of the cook to first recover the "mother" black liquor, hot and rich in residual sulfur, in one accumulator and then to recover the portion of black liquor contaminated by wash filtrate and lower in solids and temperature in another accumulator. The accumulated black liquors are then reused in reverse order to impregnate and react with, respectively, the next batch of wood chips prior to finalization of the cook with hot white liquor (Hiljanen, Tikka, EP-B 520 452). By this means it has become possible to start a kraft cook with a high charge of hydrosulfide and a low concentration of hydroxyl ion and thus carry out sulphur-lignin reactions in the hot black liquor pretreatment phase. The required causticized cooking liquor with high hydroxyl ion content, white liquor, is not charged until the finalizing cooking phase, where the hydroxyl ions are consumed, leaving the white liquor's hydrosulfide in the residual of the spent black liquor to be reused in the following batch. So far, both heat and chemicals of batch cooking can be reused very effectively by using displacement batch cooking technology.

[0008] As far as the total chemical balance of a modern kraft pulp mill is concerned, a new concept is emerging: Instead of purchasing caustic from outside, it should be produced within the chemical system of the mill. This is getting more and more important, since the developing bleaching processes use less chlorine and much more caustic than before. Declining chlorine/alkali industry, the rising cost of caustic and the mills' problems to maintain chemical balance, requiring significant external sodium input, will make the integrated alkali production a must for some pulp mills.

The solution to the above is to produce pure caustic, NaOH, on-site for the pulp mill's needs by diverting part of the green liquor to a process for carbonate crystallization and preparing pure caustic by causticizing the separated carbonate crystals. The remaining mother liquor contains residual carbonate, but also all the sulfide originally present in the green liquor. This mother liquor has now found its new use directly, as such, in improving the displacement kraft batch cooking by introduction into the front-end of the cook. Earlier it has been suggested to causticize this mother liquor separately for preparing high sulfidity white liquor, but this would have further complicated the pulp mill process. A typical situation in a modern mill producing bleached kraft pulp would require the amount of green liquor for crystallization to be set to 20% of the total green liquor production after the recovery boiler (the remaining 80% were to be causticized conventionally to white liquor for cooking). This would generate pure caustic for bleaching, corresponding to 25 kg of NaOH per ton of oven-dry wood, i.e. approximately 60 kg NaOH per air-dry metric ton of pulp, covering typically the caustic consumption of the oxygen bleaching and alkaline extraction stages. The resulting crystallization mother liquor volume for use in cooking would be 0.11 liq-to-wood units having 16 kgEA(NaOH)/kg wood and 0.23 mol HS/kg wood. Naturally, the green liquor split and the amount of pure caustic production can vary case-by-case.

## SUMMARY OF THE INVENTION

[0009] Now it has been discovered that by adding a small amount of uncausticized cooking liquor (green liquor, or a derivative thereof, such as mother liquor from green liquor carbonate crystallization) into the front-end of the black liquor recirculating displacement kraft batch process (i.e. in the impregnation and/or hot black liquor pretreatment stages), the pulping performance can be improved in terms of a facilitated cooking phase using less white liquor than would otherwise be required, improved pulp strength and bleachability. Using green liquor is very practical, since it is always available in a pulp mill. Using mother liquor from green liquor carbonate crystallization is very practical in cases,

where pure caustic for oxygen delignification and alkaline bleaching stages is made from carbonate originating from green liquor.

[0010] According to the present invention, a batch process is provided for preparing kraft pulp from lignin-containing cellulosic material, said process comprising the steps of:

- a) filling a vessel containing cellulosic material with spent cooking liquor;
- b) impregnating the cellulosic material with said spent cooking liquor;
- c) displacing said spent cooking liquor used for impregnation with another volume of spent cooking liquor and pretreating the cellulosic material;
- d) displacing the spent cooking liquor used for pretreatment with causticized cooking liquor, and cooking to a desired degree of delignification;
- e) displacing the liquor used for cooking with wash filtrate;

whereby an amount of uncausticized liquor is added at a stage prior to step d. Preferably, these additions take place prior to step a), in step a) or in step c).

#### DESCRIPTION OF THE FIGURE

[0011] Figure 1 shows a block diagram of a kraft displacement batch cooking system. The figure defines the required tanks, streams and the cooking stage sequence. To clarify the prior art displacement batch cooking technology, the following explanation is provided: The kraft batch cook is started by charging the digester with wood chips and filling the digester with black liquor AA from the impregnation black liquor tank 5, soaking the chips. An overflow, A2, to the black liquor tank 4, point AB, is preferred in order to remove air and the diluted first front of liquor. After closing the flow A2, the digester is pressurized and impregnation is completed. The cooking process is then continued by pumping in hot black liquor B from hot black liquor tank 1. The cooler black liquor A3, displaced by hot black liquor, is conducted to black liquor tank 4, point AB, discharging to an evaporation plant for recovery of cooking chemicals. The cooking sequence is continued by pumping hot white liquor C from tank 3 into the digester. The liquor D2, displaced by hot liquors above about the atmospheric boiling point, is conducted to hot black liquor tank 2. After the filling procedure described above, the digester temperature is close to the final cooking temperature. The final heating-up is carried out using direct or indirect steam heating and digester recirculation. After the desired cooking time when delignification has proceeded to the desired reaction degree, the spent liquor is ready to be displaced with wash filtrate E. In the final displacement, the first portion B1 of the displaced hot black liquor corresponds to the total of the volumes B required in the filling stages. The second portion D1 of displaced black liquor, which is diluted by the wash filtrate E but is still above its atmospheric boiling temperature, is conducted to the hot black liquor tank 2, point D. After completed final displacement, the digester contents are discharged for further processing of the pulp. The above cooking sequence may then be repeated.

[0012] The hot black liquor tank 2 provides cooled impregnation black liquor to tank 5, transferring its heat to white liquor and water by means of heat exchange.

[0013] Tank 6 is provided for storage of green liquor or a derivative thereof, supplied from the cooking chemicals recovery plant. In accordance with the present invention, at least one of portions X1 - X3 of green liquor or its derivative are introduced in the impregnation and/or pretreatment stages.

#### DETAILED DESCRIPTION OF THE INVENTION

[0014] In accordance with the present invention, improvements in the kraft pulping process have now been provided by means of a kraft batch process, which comprises the addition of uncausticized cooking liquor (green liquor) or a derivative thereof in the impregnation and pretreatment "front-end" part of the displacement kraft batch cooking process, and a finalizing delignification stage with white liquor addition, which is facilitated in terms of milder cooking conditions resulting in improved pulp quality.

[0015] In the following, reference is made to the figure described in the preceding section.

[0016] In accordance with one embodiment of the process of the present invention, a volume X1 of 0.2 - 1.0 l green liquor/kg oven dry wood, corresponding to 0.15 - 0.7 mol HS/kg oven dry wood is added from tank 6 into the impregnating warm black liquor AA from the tank 5, before carrying out impregnation using a temperature of between about 90 and 110 °C and a time of between about 30 - 60 min.

[0017] In accordance with a second embodiment of the process of the present invention, a volume X2 of 0.2 - 1.0 l green liquor/kg oven dry wood, corresponding to 0.15 - 0.7 mol HS/kg oven dry wood, is first added from tank 6 as such into the digester, followed by the warm black liquor AA for impregnation, and the impregnation is carried out using a temperature of between about 80 and 100 °C and a time of between about 30 - 60 min.

[0018] In accordance with a third embodiment of the process of the present invention, the warm black liquor impregnation is carried out as described in the prior art, and then a volume X3 of 0.2 - 1.0 l green liquor/kg oven dry wood, corresponding to 0.15 - 0.7 mol HS/kg oven dry wood is added from tank 6 into the hot black liquor B, and the hot black liquor treatment is carried out using a temperature of between 145 and 165 °C and a time between about 15 and 30 min.

[0019] In accordance with a fourth embodiment of the process of the present invention, a volume X1 of mother liquor from green liquor crystallization, 0.06 - 0.4 l/kg oven dry wood, corresponding to 0.15 - 0.7 mol HS/kg oven dry wood, is added from tank 6 into the impregnating warm black liquor AA and the impregnation is carried out using a temperature of between about 90 and 110 °C and a time of between about 30 - 60 min.

[0020] In accordance with a fifth embodiment of the process of the present invention, a volume X2 of mother liquor from green liquor crystallization, 0.06 - 0.4 l/kg oven dry wood, corresponding to 0.15 - 0.7 mol HS/kg oven dry wood, is first added from tank 6 as such into the digester, followed by the warm black liquor AA for impregnation, and the impregnation is carried out using a temperature of between about 80 and 100 °C and time of between about 30 - 60 min.

[0021] In accordance with a sixth embodiment of the process of the present invention, the warm black liquor impregnation is carried out as described in prior art, and then a volume X3 of mother liquor from green liquor crystallization, 0.06 - 0.4 l/kg oven dry wood, corresponding to 0.15 - 0.7 mol HS/kg oven dry wood is added from tank 6 into the hot black liquor and the hot black liquor treatment is carried out using a temperature of between 145 and 165 °C and a time between about 15 and 30 min.

[0022] If the uncausticized cooking liquor is added at the impregnation stage of the process, a higher temperature has to be used than in the prior art in order to use the chemicals effectively and to avoid too high a residual alkali concentration in the feed to the evaporation plant. The required higher impregnation temperature is achieved by using either digester recirculation and direct or indirect steam heating, or by co-adding a small amount of hot black liquor B from tank 1 into the impregnating black liquor AA.

[0023] If the uncausticized cooking liquor is added in the hot black liquor, the temperature of this liquor is high enough to provide the desired reaction temperature.

[0024] The principal advantage of the process of the present invention is that the "front-end" of the kraft displacement batch cooking is rendered more effective. This improves pulp quality, as digestion with white liquor in the "back-end" of kraft displacement batch cooking is greatly facilitated, requiring milder back-end cooking conditions and resulting in improved pulp quality in terms of pulp strength and easier bleaching of the pulp.

[0025] Further, implementation of the process according to the present invention is advantageous for at least the following reasons:

- Unlike in the prior art, no extra cooking steps are required in the cooking sequence. Implementing the present invention does not require a break in production, since existing cooking steps are only modified and no significant equipment reconstruction is necessary. Due to the improved cooking stage, the demand for white liquor decreases and the shortened cooking time results in increased production.
- The required amount of uncausticized liquor as green liquor is small enough to be handled by a conventionally dimensioned evaporation system. The total load of the recovery system does not increase corresponding to the increased use of green liquor, as the usage of causticized cooking liquor decreases.
- The use of mother liquor from green liquor carbonate crystallization is very advantageous in view of the chemical balance of a modern kraft pulp mill. Causticizing the separated carbonate on-site produces pure caustic which is needed in modern bleaching of kraft pulp. The amount of caustic purchased from outside decreases significantly and the chemical balance is maintained.

[0026] The following examples are illustrative of the invention and make clear the advantages over the prior art kraft batch displacement cooking with black liquor front-end.

[0027] The following abbreviations are used in the examples:

EA	Effective alkali = NaOH + ½ Na <sub>2</sub> S, expressed as NaOH equivalents
AA	Active alkali = NaOH + Na <sub>2</sub> S, expressed as Na <sub>2</sub> O equivalents
WBL	Warm impregnation black liquor
OWBL	Over flown WBL
DWBL	Displaced (out) WBL
HBL	Hot black liquor
RHBL	Displaced (out) HBL
WL	White liquor, causticized cooking liquor

(continued)

DL	Terminal displacement liquor
GL	Uncausticized cooking liquor, "green liquor"
xGL	Mother liquor from carbonate crystallization of GL
O	Oxygen delignification step
D	Chlorine dioxide bleaching step
E	Alkali extraction step

[0028] The results and advantages of the present invention are summarized in the following table.

Table 2. Result summary of the examples. All experiments have been cooked to a constant kappa number 20 and cook end point residual EA of 20 gEA/l.

Parameter	Reference	Method	Method	Method
	Example 1	Example 2	Example 3	Example 4
Additional liquor	No	GL	GL	xGL
Charge (liq-to-wood units)	No	0.5	0.5	0.11
White liquor charge (\$EA on ODwood)	20.7	16.3	17.1	17.3
H-factor demand	1006	980	1008	978
Screened yield (%)	43.6	43.4	43.4	43.2
Viscosity (ml/g)	1052	1041	1081	1035

Table 2, cont'd

Parameter	Reference Example 1	Method Example 2	Method Example 3	Method Example 4	Method Example 5
Unbleached pulp strength, tear index at tensile 90 mN/g (mNm <sup>2</sup> /g)	14.7	16.2	16.2	15.8	16.4
Active Chlorine consumption multiple at 89 % (ISO) (kg act.Cl/ODtxkappa)	4.2	4.2	3.7	3.8	3.7
Brightness ceiling (% ISO)	90.1	90.1	90.5	90.3	90.9
Bleached pulp strength, tear index at tensile 90 mN/g (mNm <sup>2</sup> /g)	14.0	15.0	16.4	15.3	16.4

[0029] Based on the results in table X, the present invention offers the following surprising benefits over a similar



state-of-the-art cooking process:

[0030] By using a small volume of uncausticized cooking liquor in the front-end of the displacement kraft batch cooking according to methods presented in examples 2 through 5,

- 5 - the charge of causticized strongly alkaline cooking liquor, i.e. white liquor, can be decreased by 20 % while maintaining unchanged pulp yield, viscosity and H-factor demand, i.e. cooking time,
- the strength of unbleached pulp increases by 10 %,
- 10 - the bleaching chemical consumption decreases by 10 %,
- the brightness ceiling, i.e. the highest achievable brightness, increases,
- and the pulp strength advantage retains over the bleaching of the pulp.

#### EXAMPLE 1

Production of a normal "reference" pine kraft pulp by using the displacement kraft batch technique

20 [0031] 3.5 kg pine (*Pinus sylvestris*) chips (oven dry basis) were metered into a chip basket positioned in a 20-liter jacketed displacement batch digester with forced circulation. The cover of the digester was closed and chips were steamed 10 minutes at 100 °C under atmospheric pressure. Impregnation black liquor (WBL, 80-90 °C, 8 gEA/l) was pumped in during 20 minutes with some overflow (OWBL) followed by impregnation at 80 °C under 5 bar pressure for 20 minutes. After impregnation, a hot black liquor pre-treatment stage followed by introducing hot black liquor (HBL, 25 165 °C, 20 gEA/l) to the bottom of the digester displacing the spent impregnation black liquor out from the top of the digester (DWBL). After the 20 min hot black liquor stage, hot white liquor (105 gEA(NaOH)/l; Sulfidity 40 %) charge was introduced to the bottom of the digester displacing the corresponding volume of spent hot black liquor out of the digester top (RHBL). A 25 minutes heating-up with circulation raised the temperature from 155 °C to the cooking temperature of 170 °C. After the desired cooking time fulfilled the target H-factor, terminal displacement was started 30 by introducing washing buffer solution DL (0.02 Mol Na<sub>2</sub>CO<sub>3</sub>/l + 0.05 Mol Na<sub>2</sub>S/l) into the digester bottom displacing the hot spent black liquor out of the digester top. The first displaced portion of the hot black liquor (HBL 1) covered the 17 l volume needed for the next cook's hot black liquor charge. The second portion of the displaced liquor (BL 2) covered the 13 l volume needed for getting the temperature down and for the next cook's impregnation liquor. After the terminal displacement, the pulp was disintegrated, washed with deionized water, screened and analyzed. This 35 cooking procedure was repeated three times by reclaiming the displaced liquors into the next cook. By these means, an equilibrium in the cooking process was obtained and the cooks started to repeat themselves corresponding to the industrial batch cooking system. In all cooking experiments, the cooking conditions were adjusted so that the resulting kappa number was 20 and the residual EA at the end of the cooking stage was 20 gEA/l. The table E1.1. below lists the liquor inputs and outputs (volumes in liters) and the conditions in corresponding cooking stages. The unbleached 40 pulp was analyzed in terms of total yield, screened yield, kappa number, viscosity, brightness and pulp strength by beating and testing. In addition, unbleached pulp was bleached with the bleaching sequence O-D-Eop-D-E-D. Bleaching chemicals demand for a given pulp brightness was determined and the pulp strength measured by beating and testing. Bleaching process conditions are given in table E1.2. Cooking characteristics and results are given in table E1.3.

Table E1.1.

Liquor inputs and outputs and corresponding cooking stage conditions in Example 1. Volumes in liters.		
Liquor in	Liquor out	Process stage
WBL 30.7	OWBL 12	Warm black liquor impregnation 80 °C, 40 min
HBL 13.3	DWBL 13.5	Hot black liquor pretreatment 155 °C, 20 min
HWL, According to charge apr. 7 + 3.5 HBL	RHBL apr. 10	Hot white liquor fill
DL 30	HBL 17 BL 2 13	Terminal displacement

Table E1.2.

Bleaching process conditions in all examples.						
Stage	O	D0	Eop	D1	E	D2
Time(min)	90	30	120	180	90	240
Temperature(°C)	105	60	70	75	60	75
Consistency(%)	10	10	12	12	12	12
Pressure(bar)	6(O <sub>2</sub> )	atm	2(O <sub>2</sub> )	atm	atm	atm
NaOH(%)	1.1-1.2	-	0.6xD0 Act.Cl	-	0.5	-
MgSO <sub>4</sub> (%)	0.5	-	-	-	-	-
ClO <sub>2</sub> ,Act.Cl(%)	-	0.2	-	varied	-	varied
H <sub>2</sub> O <sub>2</sub> (%)	-	-	0.3	-	-	-
End-pH	11	2	-	3.5-4	-	3.5-4
Kappa red. (%)	40-45	-	-	-	-	-

Table E1.3.

Results of Example 1.	
<b>Cooking</b>	
Charge uncausticized cooking liquor, as (liquor-to-wood units)	0
as (TA, total alkali(NaOH))	0
White liquor charge (EA, %(NaOH))	20.7
H-factor	1006
Kappa number	20
Cooking residual (gEA(NaOH)/l)	20
Screened Yield (%)	43.6
SCAN Viscosity (ml/g)	1052
ISO Brightness (%)	34.0
Tear Index at Tensile Index 90 Nm/g (mNm <sup>2</sup> /g)	18.3
<b>Bleaching</b>	
Act. chlorine consumption multiple for 89%(ISO) brightness, (kg act.Cl/(ODtonxkappa))	4.2
Brightness ceiling (%ISO)	90.1
SCAN Viscosity at ISO89% Brightness (ml/g)	765
Tear Index at Tensile Index 90 Nm/g (mNm <sup>2</sup> /g)	14

## EXAMPLE 2.

[0032] The experiment was carried out as disclosed in Example 1, but 0.5 liq-to-wood units uncausticized cooking liquor was used as described below:

[0033] After chip steaming a new liquor sequence was introduced for the impregnation: First, 18.7 l WBL (90°C) was added and then, 0.5 liq-to-wood units (1.75 l) uncausticized cooking liquor GL (90 °C) together with 3.5 l HBL (168 °C) was added. Hot black liquor was used here in order to increase the impregnation temperature to 100 °C. Table E2.1. lists the liquor volumes and conditions. Filling the liquors took 20 minutes followed by impregnation at 100 °C and 5 bar for 40 min with running the digester circulation. Because of the reduced WBL amount, 18.7 l, the WBL comprised only RHBL and the BL 2, second portion of the terminal displaced liquor. Improved results with respect to reference example 1 are given in table E2.2.

Table E2.1.

Liquor inputs and outputs and corresponding cooking stage conditions in Example 2. Volumes in liters.		
Liquor in	Liquor out	Process stage
WBL 18.7 GL 1.75 HBL 3.5	OWBL 5.25	Warm black liquor impregnation 90/100 °C, 60 min
HBL 13.3	DWBL 13.5	Hot black liquor pretreatment 155 °C, 20 min
HWL; According to charge apr. 7 + 3.5 HBL	RHBL apr. 10	Hot white liquor fill
DL 30	HBL 1 17 BL 2 13	Terminal displacement

Table E2.2.

Results of Example 2.	
<b>Cooking</b>	
Charge uncausticed cooking liquor, as (liquor-to-wood units)	0.5
as (% TA, total alkali(NaOH))	9
White liquor charge (EA, %(NaOH))	16.3
H-factor	980
Kappa number	20
Cooking residual (gEA(NaOH)/l)	20
Screened Yield (%)	43.4
SCAN Viscosity (ml/g)	1041
ISO Brightness (%)	33.9
Tear Index at Tensile Index 90 Nm/g (mNm <sup>2</sup> /g)	16.2
<b>Bleaching</b>	
Act.Chlorine consumption multiple for 89%(ISO) brightness, (kg act.Cl/(ODtonxkappa))	4.2
Brightness ceiling (%ISO)	90.1
SCAN Viscosity at ISO89% Brightness (ml/g)	763
Tear Index at Tensile Index 90 Nm/g (mNm <sup>2</sup> /g)	15

**EXAMPLE 3.**

**[0034]** The experiment was carried out as disclosed in Example 1, but 0.5 liq-to-wood units uncausticized cooking liquor was used as described below:

**[0035]** After chip steaming, a new liquor sequence was introduced for the impregnation: Before introducing any WBL, the 0.5 liq-to-wood unit portion (1.75 l) of uncausticized cooking liquor GL (90 °C) was introduced into the bottom of the digester in 10 minutes followed by introduction of 23 l of WBL in 20 min; followed by impregnation at 90 °C and 5 bar for 30 min with running the digester circulation. Table E3.1. lists the liquor volumes and conditions. Instead of a mixture of WBL+GL, the GL has the first contact with the steamed chips and it may impregnate in a less dilute environment. Improved results with respect to reference example 1 are given in table E3.2.

Table E3.1.

Liquor inputs and outputs and corresponding cooking stage conditions in Example 3. Volumes in liters.		
Liquor in	Liquor out	Process stage
GL 1.75	OWBL 6	Warm black liquor impregnation 90 °C, 60 min
WBL 23	DWBL 13.5	Hot black liquor pretreatment 155 °C, 20 min
HBL 13.5	RHBL apr. 10	Hot white liquor fill.
HWL, According to charge apr. 7 + 3.5 HBL	HBL 1 17 BL 2 13	Terminal displacement
DL 30		

Table E3.2.

Results of Example 3.	
<b>Cooking</b>	
Charge uncausticed cooking liquor, as (liquor-to-wood units)	0.5
as (% TA, total alkali(NaOH))	9
White liquor charge (EA, %(NaOH))	17.1
H-factor	1008
Kappa number	20
Cooking residual (gEA(NaOH)/l)	20
Screened Yield (%)	43.4
SCAN Viscosity (ml/g)	1081
ISO Brightness (%)	34.0
Tear Index at Tensile Index 90 Nm/g (mNm <sup>2</sup> /g)	16.2
<b>Bleaching</b>	
Act.Chlorine consumption multiple for 89%(ISO) brightness, (kg act.Cl/(ODtonxkappa))	3.7
Brightness ceiling (%ISO)	90.5
SCAN Viscosity at ISO89% Brightness (ml/g)	813
Tear Index at Tensile Index 90 Nm/g (mNm <sup>2</sup> /g)	16.4

**EXAMPLE 4.**

**[0036]** The experiment was carried out as disclosed in Example 1, but 0.5 liq-to-wood units uncausticized cooking liquor was used as described below:

**[0037]** The impregnation part of the process was carried out as described in Example 1, but the volume of WBL was 24 l. The 0.5 liq-to-wood units (1.75 l) of GL, uncausticized cooking liquor, was introduced into the hot black liquor pretreatment, together with the hot black liquor. In all other respect, the process was as in Example 1. Table E4.1. lists the liquor volumes and conditions. Improved results with respect to reference example 1 are given in table E3.2.

Table E4.1.

Liquor inputs and outputs and corresponding cooking stage conditions in Example 4. Volumes in liters.		
Liquor in	Liquor out	Process stage
WBL 24	OWBL 5	Warm black liquor impregnation 80 °C, 40 min
HBL 13.3	DWBL 15.5	Hot black liquor pretreatment 155 °C, 20 min
GL 1.75		Hot white liquor fill
HWL, According to charge apr. 7		
+ 3.5 HBL	RHBL apr. 10	
DL 30	HBL 1 17	Terminal displacement
	BL 2 13	

Table E4.2.

Results of Example 4.	
<b>Cooking</b>	
Charge uncausticed cooking liquor, as (liquor-to-wood units)	0.5
as (% TA, total alkali(NaOH))	9
White liquor charge (EA, %(NaOH))	16.5
H-factor	1017
Kappa number	20
Cooking residual (gEA(NaOH)/l)	20
Screened Yield (%)	43.9
SCAN Viscosity (ml/g)	1088
ISO Brightness (%)	33.5
Tear Index at Tensile Index 90 Nm/g (mNm <sup>2</sup> /g)	15.8
<b>Bleaching</b>	
Act.Chlorine consumption multiple for 89%(ISO) brightness, (kg act.Cl/(ODtonxkappa))	3.8
Brightness ceiling (%ISO)	90.3
SCAN Viscosity at ISO89% Brightness (ml/g)	786
Tear Index at Tensile Index 90 Nm/g (mNm <sup>2</sup> /g)	15.3

**EXAMPLE 5.**

**[0038]** The experiment was carried out as disclosed in Example 1, but uncausticized mother liquor from carbonate crystallization of the GL was used as described below:

**[0039]** After steaming the chips a new liquor sequence was introduced for the impregnation: Before introducing any WBL, the 0.11 liq-to-wood units portion of uncausticized mother liquor xGL (0.39 l, 90 °C) was introduced into the bottom of the digester in 10 minutes followed by introduction of 23 l of WBL in 20 min; followed by impregnation at 90 °C and 5 bar for 30 minutes with running the digester circulation. Table E5.1. lists the liquors and conditions. Improved results with respect to reference example 1 are given in table E5.2.

Table E5.1.

Liquor inputs and outputs and corresponding cooking stage conditions in Example 5. Volumes in liters.		
Liquor in	Liquor out	Process stage
xGL 0.39		

Table E5.1. (continued)

Liquor inputs and outputs and corresponding cooking stage conditions in Example 5. Volumes in liters.		
Liquor in	Liquor out	Process stage
WBL 23	OWBL 5	Warm black liquor impregnation 90 °C, 60 min
HBL 13.5	DWBL 13.5	Hot black liquor pretreatment 155 °C, 20 min
HWL, According to charge apr. 7 + 3.5 HBL	RHBL apr. 10	Hot white liquor fill
DL 30	HBL 1 17 BL 2 13	Terminal displacement

Table E5.2.

Results of Example 5.	
Cooking	
Charge uncausticed GL chrystallization mother, liquor, as (liquor-to-wood units)	0.11
as (% TA, total alkali(NaOH))	2.9
White liquor charge (EA, %(NaOH))	17.3
H-factor	978
Kappa number	20
Cooking residual (gEA(NaOH)/l)	20
Screened Yield (%)	43.2
SCAN Viscosity (ml/g)	1035
ISO Brightness (%)	31.4
Tear Index at Tensile Index 90 Nm/g (mNm <sup>2</sup> /g)	16.6
Bleaching	
Act.chlorine consumption multiple for 89%(ISO) brightness, (kg act.Cl/(ODtonxkappa))	3.7
Brightness ceiling (%ISO)	90.9
SCAN Viscosity at ISO89% Brightness (ml/g)	773
Tear Index at Tensile Index 90 Nm/g (mNm <sup>2</sup> /g)	16.4

### Claims

1. A batch process for preparing kraft pulp from lignin-containing cellulosic material, comprising the steps of:
  - a) filling a vessel containing cellulosic material with spent cooking liquor;
  - b) impregnating the celulosic material with said spent cooking liquor;
  - c) displacing said spent cooking liquor used for impregnation with another volume of spent cooking liquor and pretreating the cellulosic material;
  - d) displacing the spent cooking liquor used for pretreatment with causticized cooking liquor, and cooking to a desired degree of delignification;
  - e) displacing the liquor used for cooking with wash filtrate;

characterized in that it further comprises the addition of an amount of uncausticized liquor prior to step d.

2. The process of claim 1, characterized in that an amount of uncausticized liquor is added prior to step a).
- 5 3. The process of claim 1 or 2, characterized in that an amount of uncausticized liquor is added together with the spent cooking liquor introduced in step a).
4. The process of any claim 1-3, characterized in that an amount of uncausticized liquor is added together with the spent cooking liquor introduced in step c).
- 10 5. The process of any claim 1-4, characterized in that the amount of uncausticized cooking liquor corresponds to 0.2 to 1.0 l/kg of oven dry wood.
- 15 6. The process of any claim 1-4, characterized in that the uncausticized liquor used is mother liquor from the crystallization of carbonate from green liquor, and the amount added corresponds to 0.06 to 0.4 l/kg of oven dry wood.

#### Patentansprüche

- 20 1. Batch-Verfahren zur Herstellung von Kraft-Zellstoff aus ligninhaltigem Cellulosematerial mit den Schritten:
  - a) Befüllen eines das Cellulosematerial enthaltenden Behälters mit Kochablauge,
  - b) Imprägnieren des Cellulosematerials mit Kochablauge,
  - 25 c) Verdrängen der zur Imprägnierung verwendeten Kochablauge durch ein weiteres Volumen Kochablauge und Vorbehandlung des Cellulosematerials,
  - d) Verdrängen der zur Vorbehandlung verwendeten Kochablauge durch kaustifizierte Kochlauge und Kochen bis zum gewünschten Grad der Delignifizierung;
  - e) Verdrängen der zum Kochen verwendeten Lauge durch Waschlösung;
- 30 dadurch gekennzeichnet, daß das Verfahren zusätzlich den Schritt der Zugabe einer Menge unkaustifizierter Lauge vor Schritt d enthält.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß eine Menge unkaustifizierter Lauge vor Schritt a) zugegeben wird.
- 35 3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß eine Menge unkaustifizierter Lauge zusammen mit der in Schritt a) eingeleiteten Kochablauge zugegeben wird.
4. Verfahren nach einem der Ansprüche 1-3, dadurch gekennzeichnet, daß die Menge unkaustifizierter Lauge gemeinsam mit der in Schritt c) eingeführten Kochablauge zugesetzt wird.
- 40 5. Verfahren nach einem der Ansprüche 1-4, dadurch gekennzeichnet, daß die Menge unkaustifizierter Kochlauge 0,2 to 1,0 l/kg ofentrockenem Holz entspricht.
- 45 6. Verfahren nach einem der Ansprüche 1-4, dadurch gekennzeichnet, daß die unkaustifizierte Lauge die zur Kristallisation des Carbonats aus der Grünlauge verwendete Mutterlauge ist und die zugesetzte Menge 0,06 bis 0,4 l/kg ofentrockenem Holz entspricht.

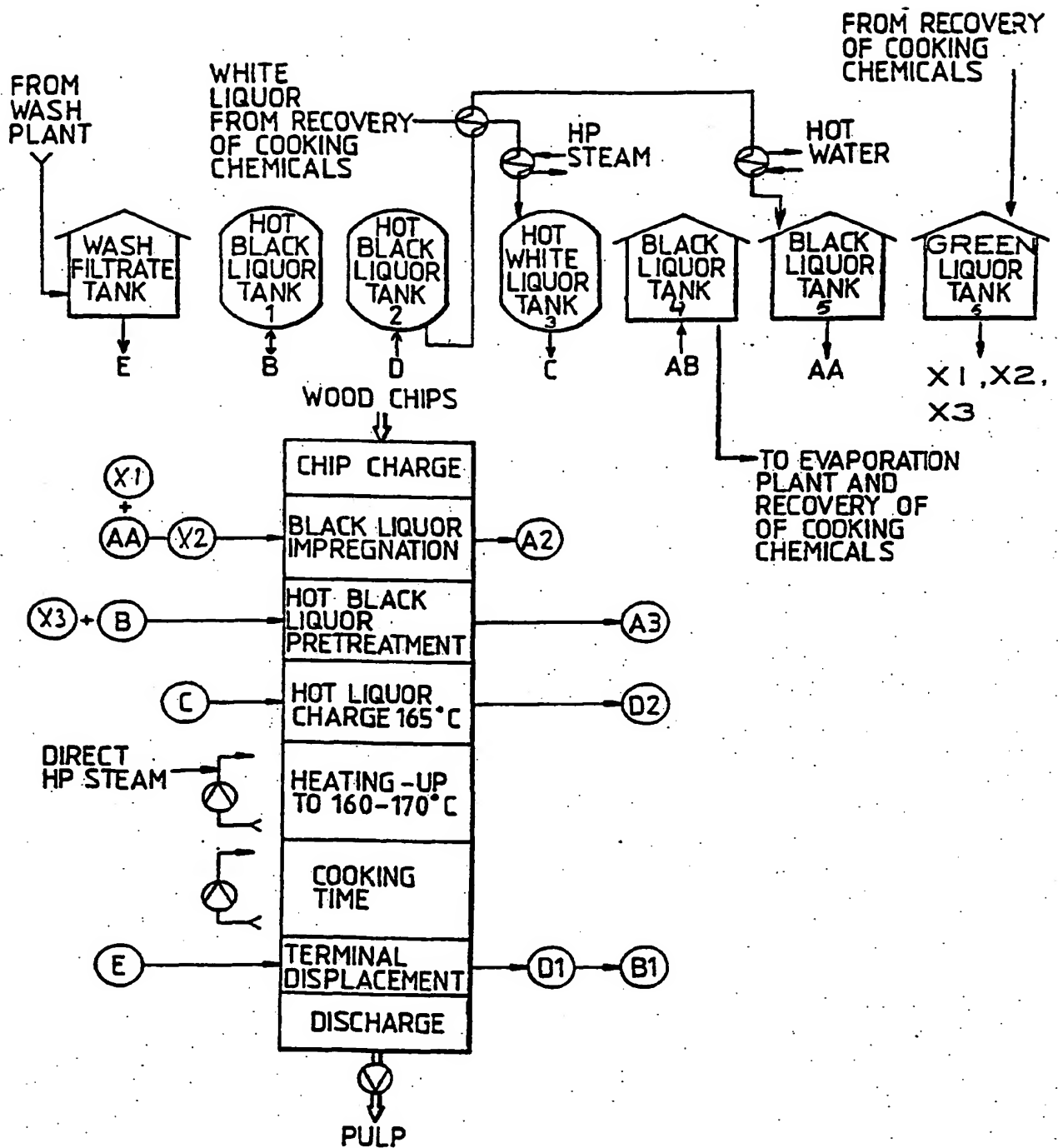
#### Revendications

- 50 1. Procédé par lots pour la préparation de pâte kraft à partir d'un matériau cellulosique contenant de la lignine, comprenant les étapes de :
  - 55 a) remplissage d'un récipient contenant le matériau cellulosique avec une liqueur de cuisson épuisée ;
  - b) imprégnation du matériau cellulosique par ladite liqueur de cuisson épuisée ;
  - c) déplacement de ladite liqueur de cuisson épuisée utilisée pour l'imprégnation par un autre volume de liqueur de cuisson épuisée, et pré-traitement du matériau cellulosique ;

- d) déplacement de la liqueur de cuisson épuisée utilisée pour le pré-traitement par une liqueur de cuisson caustifiée, et cuisson jusqu'à un degré souhaité de délignification ;
- e) déplacement de la liqueur utilisée pour la cuisson par un filtrat de lavage ;

- 5 caractérisé en ce qu'il comprend en outre l'addition d'une quantité de liqueur non caustifiée avant l'étape d).
- 2. Procédé selon la revendication 1, caractérisé en ce qu'une quantité de liqueur non caustifiée est ajoutée avant l'étape a).
  - 10 3. Procédé selon la revendication 1 ou 2, caractérisé en ce qu'une quantité de liqueur non caustifiée est ajoutée à la liqueur de cuisson épuisée introduite lors de l'étape a).
  - 4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce qu'une quantité de liqueur de cuisson non caustifiée est ajoutée à la liqueur de cuisson épuisée introduite lors de l'étape c).
  - 15 5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que la quantité de liqueur de cuisson non caustifiée correspond à 0,2 à 1,0 litre/kg de bois séché en étuve.
  - 20 6. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que la liqueur non caustifiée utilisée est une liqueur mère obtenue à partir de liqueur verte après cristallisation du carbonate qui y est contenu, et en ce que la quantité ajoutée correspond à 0,06 à 0,4 litre/kg de bois séché en étuve.





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